

5

**Shear Thinning Vinyl Acetate Based Polymer Latex Composition,  
especially for Adhesives**

10

**Background of the Invention**

Polymer emulsions or polymer latices prepared by conventional emulsion homo- or  
co-polymerization of vinyl acetate using polyvinyl alcohol as protective colloid are widely  
used for adhesives. There are several application fields for such emulsions such as in  
wood glues, paper and packaging adhesives (e.g. case sealing, book binding, bag making,  
card board lamination), parquet adhesives and others. Most importantly these latices are  
used in paper and packaging or in woodworking adhesive formulations or wood glues.

All these adhesives and especially woodworking adhesives are optimized with re-  
spect to several properties such as water resistance of the bond, heat resistance of the bond  
and creep of the bond. Further, before application several dispersion properties must be  
met. These are compatibility with formulation aids such as film forming agents, fillers,  
metal salts; rheological properties; storage stability; the setting speed and so on.

Vinyl acetate (VAc) based polymer latices for paper and packaging have to meet  
certain requirements regarding setting speed, penetration into the paper, open time, cohe-  
sion of the bond. On the other hand they should possess good re-dispersability of a film to  
provide good machine cleaning properties.

VAc based polymer latices for woodworking adhesives having good water resis-  
tance typically use some functional post-crosslinking co-monomer in polymerization and  
the formulation with a catalyst after polymerization. Amongst the post-crosslinkers N-  
alkylol derivatives of an amide of an  $\alpha,\beta$ -ethylenically unsaturated carboxylic acid, such as  
N-methylol acrylamide (NMA) which is preferred for latex wood glues are known. For  
example, US-A-5,439,960 and US-A-5,391,608 describe the use of 0.1 to 6% of NMA

based on total monomer content. Likewise European Patent Application EP-A-0,561,221 describes the use of 2 to 10% NMA.

5 As the catalyst for formulation of the above woodworking adhesives having good water resistance water-soluble metal salts of monobasic acids such as aluminum(III), chromium and/or zirconium(IV) salts, especially aluminum nitrate, chromium chloride or zirconium oxychloride are used (see for example DE-26,20,738, EP-A-0,433,957, EP-A-0,501,174, EP-A-0,686,683 and US-A-5,434,216).

10 Another approach to improve water resistance of wood glues is for example disclosed in EP-A-0,433,957, EP-A-0,623,661 and JP-06,322,337 which documents relate to use of more hydrophobic co-monomers such as vinyl pivalate, diisopropyl maleate, diisopropyl fumarate, vinyl chloride or versatic acid vinyl esters for this purpose.

15 Adhesive performance of for example a wood glue is typically controlled by the amount of polyvinyl alcohol, i.e. the ratio of polyvinyl alcohol to monomer, the polyvinyl alcohol molecular weight and its degree of hydrolysis as for example disclosed in US-A-5,434,216. In addition, functionalized polyvinyl alcohols, e.g. acetoacetylated polyvinyl alcohols or itaconic acid-modified polyvinyl alcohols, or ethylene modified PVOH may be  
20 used.

The choice of the polyvinyl alcohol (PVOH) determines other properties of the vinyl acetate latex and thus the adhesive obtained, especially its rheological properties such as viscosity and shear thinning, or the setting speed. Rheology mainly depends on the molecular weight distribution and degree of hydrolysis of the polyvinyl alcohol used, but can  
25 be changed by altering product recipe. For example, EP-A-0,686,683 discloses altering the rheological properties by altering the formulation with some thickening agent, thereby changing the continuous phase viscosity, at the expense of an altered recipe.

30 EP 00 114 097.9, assigned to Air Products Polymers LP, discloses adjustment of rheological properties and especially reduction of shear thinning of a latex emulsion by increasing particle size of the polymer without changing overall composition. More in detail, the document teaches increasing particle size by carrying out emulsion polymeriza-

tion of vinyl acetate and optional co-monomers in presence of a pre-crosslinking monomer selected from ethylenically unsaturated monomers such as triallyl cyanurate and allyl methacrylate. The document is silent on the possibility of increasing shear thinning factor.

5           With the term shear thinning the phenomenon of a viscosity drop with increased shear rate is addressed. Such decrease of viscosity is considered reversible if viscosity reaches the original value when the shear rate is decreased to its original value.

10           Shear thinning can be quantified by the so called "shear thinning factor" (SF) which is obtained as the ratio of viscosity measured by Brookfield viscosimeter at 1 rpm, Bf(1), and at 10 rpm, Bf(10):

$$SF = ((Bf1 / Bf10) - 1).$$

15           A shear thinning factor below zero ( $SF < 0$ ) indicates shear thickening, a shear thinning factor of zero ( $SF = 0$ ) indicates Newtonian behavior and a shear thinning factor above zero ( $SF > 0$ ) stands for shear thinning behavior. Shear thinning factors  $\neq 0$  reflect properties of emulsions with high solids content as is typically the case for VAc based latices. Non-Newtonian behavior is in general no problem at lower solids contents (e.g. below 40  
20   %).

25           It is an object of the present invention to find a possibility for independent control of the shear thinning factor which in turn allows to precisely and intentionally adapt the emulsion or latex for certain applications thereby improving performance of for example a paper and packaging adhesive or of a woodworking adhesive or wood glue.

30           In several cases it would be especially useful and desirable to control shear thinning i.e. the shear thinning factor and to provide the desired extend of it. More specifically, it would in the first place be desirable to avoid any shear thickening i.e. to be in the position to shift the shear thinning factor from negative to positive values ( $SF > 0$ ). Performance requirements for a paper and packaging adhesive are, however, typically a SF within the range of  $0.1 < SF \leq 1.5$  dependent on the specific application, whereas performance re-

quirements for a wood glue are typically a SF in the range of  $0.1 < SF \leq 0.6$ . In any case shear thickening ( $SF < 0$ ) is preferably to be avoided.

5 Additionally, the requirements for setting speed and cohesion must be fulfilled: In the case of a paper and packaging adhesive setting speed measured as AZG in seconds should be:  $< 4$  s, whereas cohesion measured at  $70\text{ }^{\circ}\text{C}$  should be  $\geq 4\text{ N/mm}^2$ .

10 In the case of a woodworking adhesive (wood glue) the setting speed measured as bond strength after 2.5 minutes gluing time should be  $> 1.5\text{ N/mm}^2$ . Cohesion of the wood bond measured as bond strength at  $80\text{ }^{\circ}\text{C}$  should be  $> 6\text{ N/mm}^2$ .

15 Other useful adhesive performance parameters created e.g. by the level of co-monomer such as NMA, and/or by the amount of PVOH and/or by its molecular weight and hydrolysis distribution, should remain more or less unchanged.

It is thus another object of the invention to provide a wood glue which meets the above requirements and has improved water resistance.

## 20 **Brief Summary of the Invention**

The above objects are solved and the drawbacks of the prior art are overcome according to a first aspect of the invention by a vinyl acetate based polymer latex composition obtained by emulsion polymerization of:

- 25 (a) polyvinyl alcohol,  
(b) a monomer mixture comprising vinyl acetate, and optionally (d) one or more additional co-monomer(s),

in presence of (c) 0.0001 to 0.05 wt.% (1 to 500 ppm) of a chain transfer agent (CTA), based on total monomer weight, said vinyl acetate based polymer latex composition having  
30 a weight average particle size  $\geq 400\text{ nm}$  and a higher shear thinning factor than the vinyl acetate based polymer latex composition obtained in the absence of the chain transfer agent.

According to a first embodiment the emulsion polymerization is carried out in presence of 0.001 to 0.05 wt.% of a chain transfer agent selected from aldehydes, especially C<sub>2-5</sub>-aldehydes and other CTAs having a similar chain transfer constant with regard to VAc as the monomer.

According to a second embodiment the emulsion polymerization is carried out in presence of 0.0001 to 0.01 wt.% of a chain transfer agent selected from thiols, especially C<sub>2-5</sub>-thiols, mercapto acids, especially C<sub>2-5</sub>-mercapto acids and other CTAs having a similar chain transfer constant with regard to VAc as the monomer.

The latex of the invention preferably has a shear thinning factor of about 1,2 to 3,5 times the shear thinning factor of a latex composition obtained in absence of the chain transfer agent or wherein the shear thinning factor is shifted from negative values to positive values as compared to the shear thinning factor of a latex composition obtained in absence of the chain transfer agent.

Preferably, the latex weight average particle size is about 60 to 95 % the weight average particle size of a latex composition obtained in the absence of the chain transfer agent.

Preferably, the chain transfer agent is selected from the group consisting of aldehydes, preferably C<sub>2-5</sub>-aldehydes, thiols, preferably C<sub>2-5</sub>-thiols, mercapto acids, preferably C<sub>2-5</sub>-mercaptoacids, and mixtures thereof. More preferably the chain transfer agent is selected from the group consisting of acetaldehyde, croton aldehyd, propion aldehyde, 2-mercapto propionic acid, 3-mercapto propionic acid, and mixtures thereof.

The amount of vinyl acetate is preferably in the range of 100 wt.% to 60 wt.%, based on total monomer weight.

According to an especially preferred embodiment the vinyl acetate based polymer latex composition is a copolymer of vinyl acetate/N-methylol acrylamide, optionally further including versatic acid vinyl ester having 9 to 13 carbon atoms from the carbonic acid group. The chain transfer agent is then preferably a mercaptopropionic acid.

According to a second aspect the present invention relates to a process of manufacture of a vinyl acetate based polymer latex composition having a weight average particle size  $\geq 400$  nm, including emulsion polymerization of vinyl acetate in the presence of polyvinyl alcohol, optionally together with one or more additional co-monomer(s), wherein the emulsion polymerization is carried out in the presence of 0.0001 to 0.05 wt.% of a chain transfer agent, based on total monomer weight. Preferably the chain transfer agents and the amounts used are as defined above.

According to a third aspect the present invention relates to an adhesive, comprising the vinyl acetate based polymer latex composition as defined above.

According to a preferred embodiment the adhesive is for use as a fast setting adhesive for paper and packaging, said adhesive comprising a vinyl acetate homopolymer latex composition.

According to another preferred embodiment the adhesive is for use as a wood glue and comprises a vinyl acetate based polymer latex composition of a copolymer of vinyl acetate/N-methylol acrylamide, optionally further including versatic acid vinyl ester having 9 to 13 carbon atoms from the carbonic acid group. The chain transfer agent is preferably mercapto propionic acid.

### **Detailed Description of the Invention**

The present invention is based on the surprising finding that the shear thinning factor of a vinyl acetate based polymer latex prepared by conventional emulsion polymerization using PVOH as a protective colloid can be increased without substantially changing the latex composition, especially without changing the type and/or amount of PVOH. This can be achieved by polymerizing the vinyl acetate in presence of a small amount of a chain transfer agent without a significant change of the average molecular weight, measured as the K-value. Thereby other important adhesive properties, such as cohesion, remain un-

changed, whereas the shear thinning may be adjusted as desired and/or a shear thickening may be even reversed to shear thinning.

More in detail, the invention to a first aspect thereof thus relates to a vinyl acetate based polymer latex composition obtained by emulsion polymerization of:

- (a) polyvinyl alcohol,
- (b) a monomer mixture comprising vinyl acetate, and optionally (d) one or more co-monomer(s),

in presence of (c) 0.0001 to 0.05 wt.% (1 to 500 ppm) of a chain transfer agent, based on total monomer weight, said vinyl acetate based polymer latex composition having a weight average particle size  $\geq 400$  nm. The resulting VAc based polymer latex composition has a higher shear thinning factor than the VAc based polymer latex of the same composition (a), (b) and optionally (d) which is obtained in absence of the chain transfer agent (c). At the same time, the K-value indicating molecular weight is surprisingly slightly increased or remains about comparable.

The use of a chain transfer agent (CTA) in emulsion polymerization of VAc monomers is well known in the art and is described in textbooks, e.g. "Vinyl Polymerization", edited by George E. Ham, Marcel Dekker, 1967, Vol. I, Chapter 4, pages 207 - 329: M. K. Lindemann, "The Mechanism of Vinyl Acetate Polymerization" or "Vinyl Acetate Emulsion Polymerization and Copolymerization with Acrylic Monomers" by H. Y. Erbil, CRC Press 2000.

The latter textbook teaches that CTAs can be included in emulsion polymerization to terminate propagating polymer chains and to prevent polymer chains from growing too large, which may create problems in subsequent applications. Changing the concentration of such modifiers or CTAs during emulsion polymerization leads to control of average molecular weight, molecular weight distribution, branching, and crosslinking of the polymer. The extend of chain transfer can be predicted if the chain transfer constants  $C_X$  are known for a given monomer system.

Chain transfer constants  $C_X$  may be obtained as explained e.g. in the "Polymer Handbook", edited by J. Brandrup, E. H. Immergut, and E. A. Grulike, John Wiley Sons,

Inc., 4. Edition, 1999, page II/97 ff.. Various transfer constants of vinyl acetate to different species are given there. As known radical transfer of a growing polymer chain may occur to any species involved in the polymerization: monomer; polymer; protective colloid, such as PVOH; emulsifier, if used; initiator; solvent, if is used; or additives called chain transfer agents. Chain transfer constants of a certain species ( $C_X$ ), may be different by several orders of magnitude in different monomer systems.

Examples of CTAs used in VAc based latices include, but are not limited to mercaptanes/thiols, aldehydes, chlorinated aliphatics and so on. The CTAs are usually characterized by their chain transfer constant. To effect chain transfer CTAs are typically used in appreciable amounts. For example EP 0,332,175 discloses the use of chain transfer agents in emulsion polymerization of VAc based polymer latices. The specific chain transfer agents described in said document are used in an amount of 0.1 to 0.7 wt.%. The resulting polymer latices are disclosed to show an improved setting speed.

WO 01/00 695 discloses a method for radically initiated, aqueous emulsion polymerization for producing an aqueous polymer dispersion with polymer particles having a weight average particle diameter  $\leq 300$  nm. According to said method, at least one monomer with at least one ethylenically unsaturated group, preferably an acrylic monomer, is dispersed in an aqueous medium and polymerized using at least one radical polymerization initiator in the presence of at least one radical chain transfer agent ( $< 5$  wt.%) with a solubility greater than  $1 \times 10^{-5}$  mol per kilogram water at  $20^\circ\text{C}$  and at 1 bar (absolute). The resulting dispersions have a solids content of about 20 – 30 wt.%

When CTAs were used in emulsion polymerization, as given above (EP-A-0,322,175; JP-A-9,302,004; WO-A-01/00695; EP-A-0,812,863) it was accepted or it was even a goal (JP-A-9,302,004) that the molecular weight of the obtained polymer decreased. As is well known in the art, such drop of molecular weight has a negative impact on the cohesion of a bond prepared by such lower molecular weight polymer. Only in few cases, e.g. for pressure sensitive adhesives, the lower molecular weight may influence tack and adhesion in the desired direction and the resulting loss of cohesion is acceptable.



It was surprising to find that, upon use of trace amounts of a CTA, smaller final particle sizes are obtained which cause more shear thinning or which may even change a shear thickening behavior to a shear thinning one. At the same time, and even more surprisingly it was found, that latices polymerized in the presence of traces of one or more CTAs showed a clear tendency to faster setting speed.

For PVOH stabilized VAc based polymer latices, when used as adhesives, a too low molecular weight would decrease the cohesion of the bond. For these types of adhesives high cohesion is required, which should be also sufficiently high enough at higher temperatures, named then as heat resistance. CTAs are therefore generally considered disadvantageous in such compositions.

It has surprisingly and unexpectedly been discovered that the introduction of trace amounts of a CTA did not decrease the molecular weight of the resulting polymer, characterized by the K-value, but that the opposite was observed. Astonishingly, these effects can be obtained for both VAC homopolymers and VAC copolymers comprising additional co-monomers such as e.g. NMA, ethylene and/or versatic acid esters.

The chain transfer agent for use in the invention may be selected from the group consisting of aldehydes, preferably C<sub>2</sub>-C<sub>5</sub>-aldehydes, such as acetaldehyde, propion aldehyde, butyraldehyde, croton aldehyde, and n-pentanal; thiols, preferably C<sub>2</sub>-C<sub>5</sub>-thiols such as ethanthiol, propanthiol, mercaptoethanol, 2- or 3-mercaptopropanol, 1- or 2-n-butane-thiol, and n-pentanethiol; and mercaptoacids, preferably C<sub>2</sub>-C<sub>5</sub>-mercaptoacids, such as 2- or 3-mercapto propionic acid, and 2- or 3-mercapto butyric acid and mixtures thereof, mercapto acids being preferred. More preferably the chain transfer agent used in the present invention is selected from the group consisting of acetaldehyde, propion aldehyde, croton aldehyde, 2- and 3-mercapto propionic acid, and mixtures thereof. Most preferably the chain transfer agent is a mercapto propionic acid (MPA). Mixtures of CTAs may be used, provided the respective CTAs do not negatively interfere with each other.

The amount of CTA used according to the present invention is in general in the range of 0.0001 to 0.05 wt.% (1 to 500 ppm), based on total monomer content, preferably 0.001 to 0.05 wt.% (10 to 500 ppm). According to one embodiment the emulsion polym-

erization is carried out in presence of 0.001 to 0.05 wt.% (10 to 500 ppm), preferably 0.001 to 0.02 wt.% and most preferably 0.001 to 0.01 wt.%, of a chain transfer agent selected from the group consisting of aldehydes and CTAs having a similar chain transfer constant with regard to VAc as the monomer. According to an alternate embodiment the emulsion polymerization is carried out in presence of 0.0001 to 0.01 wt.% (1 to 100 ppm), preferably 0.0001 to 0.005 wt.%, and most preferably 0.001 to 0.0025 wt.%, of a chain transfer agent selected from the group consisting of thiols, mercapto acids, and CTAs having a similar chain transfer constant with regard to VAc as the monomer. All percentages are based on total monomer content. With the term "similar" as used above a chain transfer constant is addressed which with regard to VAc under polymerization conditions is in the same order of magnitude and preferably only slightly differs from the one of an aldehyde, thiol and mercaptoacid, respectively.

The resulting polymer latex has a weight average particle size of  $\geq 400$  nm. Preferably such particle size is in the range of 500 to 1500 nm, more preferably 650 to 1500 nm, most preferably 700 to 1200 nm. Solids content of the emulsion is preferably equal to or above 40 wt.%, more preferably in the range of 45 to 70 wt.%, most preferably in the range of 50 to 65 wt.%. At these high solids contents shear thinning or thickening, which is of no concern for polymer latices containing less solids ( $< 40$  wt.%), needs to be paid careful attention. The shear thinning factor can be carefully and independently adjusted by the method of the invention.

The CTA may be added to the initial reactor charge, before polymerization is started by adding the initiator, or may be fed to the reactor during the course of the polymerization. Conventional emulsion polymerization may be used as e.g. described in EP 00 114 097.9.

The polymer latex of the invention comprises vinyl acetate as the base monomer. Vinyl acetate is used in an amount of 100 to 60.0% by weight, based on total monomer content. Preferably, the amount of vinyl acetate used is in the range of 100 to 80% by weight. According to one embodiment the VAc based polymer latex may be a VAc homopolymer latex. These VAc homopolymer latices can advantageously be used for paper and packaging applications.

The VAc based latex composition may also be a co-polymer composition. In this case one or more co-monomers selected from the following may be copolymerized with VAc: one or more post-crosslinking monomer(s), one or more vinyl ester(s), one or more ethylenically unsaturated acid(s) or anhydride(s) thereof, one or more acrylic acid(s), ethylene and mixtures of the foregoing.

If e.g. designed for wood glues the vinyl acetate based polymer latex of the invention, preferably comprises a post-crosslinking monomer selected from the group consisting of N-alkylol derivatives of an amide of an  $\alpha,\beta$ -ethylenically unsaturated carboxylic acid and mixtures thereof. Preferably the post-crosslinking monomer is selected from the group consisting of N-C<sub>1-3</sub>-alkylol (meth)acrylamides, preferably N-methylol (meth)acrylamide, N-C<sub>1-3</sub>-alkylol melamides, preferably N-methylol melamide, N-C<sub>1-3</sub>-alkylol melamic acid and their esters, preferably N-methylol melamic acid, N-methylol melamic acid ester, N-C<sub>2-5</sub>-acylol amides of vinylaromatic acids, N-C<sub>1-4</sub>-alkoxymethyl (meth)acrylamide, and mixtures thereof. More preferably, the post-crosslinking monomer is N-methylol acrylamide (NMA).

With the term “(meth)acryl...” as used herein both the respective acrylic acid derivatives and the methacrylic acid derivatives are referred to. Thus, “N-methylol (meth)acrylamide” refers to both N-methylol acrylamide and N-methylol methacrylamide. The above C<sub>1-3</sub> or C<sub>1-4</sub> alkyl residues include methyl, ethyl, n-propyl, i-propyl, n-, i-, and t-butyl residues and may be chosen independently from each other.

The post-crosslinking monomer is preferably comprised in the vinyl acetate based polymer latex composition of the invention in an amount of 0.1 to 5.0% by weight based on the total monomer content. The post-crosslinking monomer or mixtures of such monomers is known to be essential for sufficient water and heat resistance of the bond. Use of such post-crosslinking monomer or monomer mixtures is therefore preferred. It is, however, not necessary to achieve the effects of the invention. Therefore, although preferred, the post-crosslinking monomer is not an essential component of the claimed latex composition.

The vinyl acetate based polymer latex composition of the invention may comprise the above one or more copolymerizable co-monomers in the following amounts: up to 40% by weight vinylic ester, up to 15% by weight acrylic monomer, up to 3% by weight unsaturated carboxylic acid, and up to 30% by weight ethylene, all percentages being based on total monomer content, or mixtures thereof, provided the total amount of copolymerizable co-monomers does not exceed 50 % by weight.

Vinyl esters other than VAc which may be used in combination with vinyl acetate are for example vinyl propionate, vinyl pivalate, vinyl laurate, vinyl 2-ethyl hexanoate, dibutyl maleate, dioctyl maleate, diisopropyl maleate, diisopropyl fumarate, versatic acid vinyl esters having 9 to 13 carbon atoms from the carbonic acid group, preferably 9 or 10 carbon atoms, or mixtures thereof. The amount of other vinyl esters, if used, is in the range of up to 40.0% by weight, based on total monomer content, preferably 3 to 30% by weight.

The acrylic monomer to be optionally comprised in the vinyl acetate based polymer latex composition of the invention may for example be selected from the group consisting of C<sub>1-8</sub>-alkyl acrylates such as ethyl acrylate, butyl acrylate, 2-ethyl hexyl acrylate or mixtures thereof. The acrylic monomer is preferably used in an amount of less than 15% by weight based on total monomer content, more preferably in an amount of 1 to 10% by weight.

The above unsaturated carboxylic acid as the co-monomer is an ethylenically unsaturated acid and may be selected from the group consisting of acrylic acid, methacrylic acid, croton acid, itaconic acid, maleic acid, fumaric acid, their anhydrides such as maleic acid anhydride, and mixtures thereof. If used, the amount of the ethylenically unsaturated carboxylic acid or their mixtures is 0.1 to 3.0 % by weight, preferably 0.5 to 2.0 % by weight, based on total monomer content.

The vinyl acetate based polymer latex composition may further comprise up to 30% by weight ethylene, preferably 1 to 20 % by weight ethylene based on total monomer contents. In a preferred embodiment, the vinyl acetate based polymer latex composition, which may optionally comprise the above post-crosslinking monomer, comprises one or both of 1 to 20 % by weight ethylene and 1 to 30% by weight vinyl ester as the copoly-

merizable co-monomers, provided the total amount of copolymerizable co-monomer does not exceed 1 to 40% by weight.

The colloidal stabilizer used in the vinyl acetate based polymer latex compositions of the invention is polyvinyl alcohol (PVOH). Various suitable polyvinyl alcohols are known to the skilled worker and are readily available. Especially preferred is a partially hydrolyzed PVOH having a degree of hydrolysis from 60 to 99 mol %, preferably from 80 to 97 mol %, most preferably 86 to 94 mol %. To achieve the desired viscosity level of the polymer latex and to allow for good adhesion performance of the bond, blends of different PVOH grades possessing different molecular weights and hydrolysis distributions may be used. The colloidal stabilizer PVOH is typically used in an amount of 3 to 15 % by weight, based on the total weight of the composition, more preferably 4 to 11 % by weight.

As put forth above, the PVOH is typically chosen to provide desired performance of the latex and/or the adhesive comprising the same, respectively. Rheological properties of the latex/adhesive likewise depend in part on the choice of the PVOH, but can be controlled independently by the use of CTAs according to the invention. This use of trace amounts of CTAs according to the invention results in reduced shear thickening, in transferring a shear thickening into a shear thinning one, or in more shear thinning i.e. in an increased of the shear thinning factor SF. Such change of rheological properties of vinyl acetate based polymer lattices using PVOH as the protective colloid, however, seemed to be impossible without changing the amount or the molecular properties of the PVOH

The polymer latex particles may be co-stabilized by use of emulsifiers, if needed. These emulsifiers are known to the skilled worker and can be included as usual. Preferably, non-ionic emulsifiers such as polyoxyethylene ethers or fatty alcohols may be used, preferably in an amount of 0.1 to 1.0% by weight, based on total monomer content.

In a second aspect the present invention relates to a process of manufacture of a vinyl acetate based latex composition having a weight average particle size  $\geq 400$  nm, including emulsion polymerization of vinyl acetate in the presence of polyvinyl alcohol, optionally together with one or more additional co-monomer(s), wherein the emulsion polymerization is carried out in the presence of 0.0001 wt.% to 0.05 wt.% of a chain transfer

agent, based on total monomer weight. The chain transfer agents(s) and the amounts used are as defined above.

The vinyl acetate based polymer latex composition of the invention may be obtained by conventional emulsion polymerization. Conventional batch or semi-batch emulsion polymerization procedures may be employed. Mainly for safety reasons and in view of the amount of heat to be dissipated, the semi-batch procedure is preferred. In case of a semi-batch procedure a certain fraction of the reactants together with some water, if desired, and some of the polyvinyl alcohol solution as well as emulsifier solution, if used, is initially charged to the reactor.

The reaction may be started by feeding an aqueous solution of the initiator or initiator components. Preferred initiation of the emulsion polymerization of the invention is carried out by a redox reaction using a redox system of an oxidant and a reductant in suitable amounts, the amount of initiator components to provide complete conversion depending on the selected initiator of the redox system. Typical oxidants are selected from the group of  $H_2O_2$ , organic hydroperoxides such as t-butyl hydroperoxide (tBHP), inorganic persulfates such as sodium persulfate, potassium persulfate and ammonium persulfate. Other organic peroxides may be used as well either alone or in combination therewith. Typical reductants are the sulfoxylates such as sodium formaldehyde sulfoxylate (SFS), sulfites such as sodium sulfite, sodium hydrogen sulfite, dithionites such as sodium dithionite, and organic reductants such as ascorbic acid and its derivatives. Preferred combinations are t-butyl hydroperoxide or hydrogen peroxide and sodium formaldehyde sulfoxylate (optionally in the presence of traces of ferro ammonium sulfate), t-BHP or  $H_2O_2$  and sodium sulfite, t-BHP or  $H_2O_2$  and sodium hydrogen sulfite, t-BHP or  $H_2O_2$  and sodium dithionite, t-BHP or  $H_2O_2$  and ascorbic acid, t-BHP or  $H_2O_2$  and erythorbic acid. Thermal initiation by  $H_2O_2$  or other peroxides may also be applied.

Preferably, initiation of the emulsion polymerization is carried out by t-BHP or  $H_2O_2$  and SFS in the presence of traces of ferro ammonium sulfate. The initiator is used in suitable amounts to provide complete conversion of the monomers. In case of the preferred initiation system typically less than 0.015% by weight t-BHP, based on total monomer content, for the course of the polymerization and less than 0.15% by weight t-BHP,

based on total monomer content, for post-polymerization to reduce the residual monomer content below 50 ppm, based on the emulsion, is used. Molar ratios of the SFS are used during the course of the polymerization, typically, but are not desired.

5 Further on, the remaining fractions of the reactants, the PVOH solution as well as the emulsifier solution, if used, and extra water, if needed, are fed over a certain period of time to the reaction vessel. Feeding rates will typically be kept constant over the feeding time, but may also vary, if desired. Typical reaction times depend on the reaction temperature and are typically within the range of 2 hours to 8 hours, preferably 4 hours to 6 hours.

10 The polymerization reaction of the invention is preferably performed at a temperature ranging from 50 to 90 °C, preferably between 60 and 80 °C, during most of the reaction time. Care has to be taken that an appropriate mixing of the components occurs in the reaction vessel. Mixing is achieved by conventional means known to the skilled worker.  
15 Initial reactor charges and procedure can be chosen as needed.

20 The initiator components will be fed to the reactor during all the reaction time, even after the feeding of reactants is finished until nearly complete conversion is reached. The initiator feeding rate may be kept constant or may vary over the time. For post-polymerization which is preferably carried out to reduce residual monomer content below 500 ppm based on the latex, more concentrated solutions of initiator components (preferably t-BHP/SFS) are fed to the latex. Finally the latex is cooled to ambient temperature.

25 Final latex viscosity at 50% solids by weight will be between 1,000 and 40,000 mPas, mainly but not only depending on the type and amount of polyvinyl alcohol used. Viscosity is measured using a Brookfield viscometer at 20 rpm at 23°C.

30 The vinyl acetate based polymer latex composition of the invention thus obtained may be formulated into an adhesive by conventional means. In a third aspect the present invention thus relates to an adhesive comprising the above VAc based polymer latex composition. Optionally such adhesive may comprise suitable additives known to the skilled worker. Examples of such additives are plasticizers, anti-blocking agents, film forming agents; water-soluble metal salts of monobasic acids such as aluminum, chromium and/or

zirconium salts; free mineral acids such as hydrochloride acid, nitric acid, perchloric acid, phosphoric acid or mixtures thereof and antifoam agents (defoamers), biocides, and so on. For the use as a water resistant wood glue the formulation with metal salts, such as aluminum, chromium and /or zirconium salts; free mineral acids, such as hydrochloric acid, phosphoric acid or mixtures thereof is preferred.

The adhesives of the invention may be characterized as follows:

Paper and packaging adhesives:

- 10 A shear thinning factor SF in the range of  $0.1 < SF \leq 1.5$  dependent on the desired application.
- A setting speed measured as AZG in seconds of  $AZG < 4$  s.
- A cohesion measured at 70 °C of  $\geq 4$  N/mm<sup>2</sup>.

15 Water resistant wood glues:

- A shear thinning factor SF in the range of  $0.1 < SF \leq 0.6$ .
- A setting speed measured as bond strength after 2.5 minutes gluing time of  $> 1.5$  N/mm<sup>2</sup>.
- A cohesion measured at 80 °C of  $> 6$  N/mm<sup>2</sup>.
- 20 Water resistance of a wood glue of performance group D3:  $D3 > 2$  N/mm<sup>2</sup> and water resistance of a wood glue of performance group D4:  $D3 \geq 4$  N/mm<sup>2</sup> and  $D4 \geq 4$  N/mm<sup>2</sup>.

Properties of latices were measured by the following test methods.

25

**Test methods**

**Latex particle size:**

Final latex particle size distributions were obtained either using the COULTER LS230, or using the COULTER N4, both supplied by Coulter Cooperation, Miami, Florida 33196. Samples of the final latex were diluted to appropriate concentration using pure distilled water.

30



Coulter LS230 measurement is based on light diffraction combined with some static light scattering and provides a particle size distribution. As the larger particles are overestimated by this instrument, the median of the volume distribution function was chosen to characterize an average particle size.

5

Coulter N4 measurement is based on dynamic light scattering detected at 90 degrees scattering angle. The weight average was used to characterize particle size. Each value was obtained as an average of 3 measurements.

10

#### **Latex viscosity and shear thinning:**

Latex viscosity was measured using Brookfield viscosimeter. Viscosity data were taken for 1, 10 and 20 RPM. The latex viscosity is given for 20 RPM (Bf 20) in mPas. To characterize the non-Newtonian behavior a shear thinning factor SF is calculated from the viscosity at 1 and 10 RPM:  $SF = (Bf1 / Bf10) - 1$ . A shear thinning factor  $SF > 0$  indicates shear thinning whereas  $SF < 0$  stands for shear thickening. All measurements were carried out at 23 °C.

15

#### **Testing of K-value:**

A latex sample was one weighed to obtain 1 gram of polymer (not including the PVOH). This sample was diluted with 5 ml of pure water. 90 ml of tetra hydrofurane (THF) were slowly added under stirring to give a clear polymer solution at room temperature. Additional pure water was then added to obtain a total amount of 100 ml solution. The viscosity of the homogeneous solution was estimated using an Ubbelohde viscosimeter. Calculation of viscosity included the Hagenbach correction. The same was carried out for a solution representing the solvent including the right amount of PVOH and 90 gram of THF. The "Eigenviscosity"  $k$  was then calculated based on the Fikentscher Equation. The K-value is then defined by  $K = 10^3 k$ . It represents a simple viscosimetric average of the polymer molecular weight.

20

25

30

#### **Wood working adhesive formulation:**

Base latices, which were polymerized as explained below, were formulated to provide the wood working adhesive formulation. Butyl carbitol acetate was used as a film forming agent (2,6 parts per 100 parts of latex). Alumium chloride hydrate was then added

as a catalyst (3.5 parts of a 50% solution per 100 parts of emulsion for testing the D3-value, or 5 parts of a 50% solution for testing the D4-values). The components were mixed at ambient temperature. The wood specimens were glued within 1 to 5 days after preparation of the formulation.

5

#### **Bond strength in accordance with DIN EN 204/205:**

Test specimens were produced in accordance with DIN EN 205. For this purpose pairs of beech wood panels, each 5 mm thick, 130 mm wide and 600 mm long, were bonded to one another with the adhesive formulation to be tested under a pressure distributed uniformly over the bond area and were stored in accordance with DIN EN 204. Following storage, the bonded panels were divided into test specimens each measuring 150 mm in length, and these test specimens were used to determine the bond strength in the tensile shear test. In this test the bonded specimens were pulled apart using a tensile testing machine at a pulling rate of 50 mm/min and were stressed until they broke. On fracture, the maximum force  $F_{max}$  which occurred at that point was determined. The bond strength  $T$  is calculated in accordance with DIN EN 205 from  $T = F_{max}/A$ , where  $A$  is the bonded test area. Results are given in  $N/mm^2$ .

For testing of allocation to performance group D3, the specimens, after gluing, were stored under standard climatic conditions (23 °C, 50 % atmospheric humidity) for 7 days and then stored in cold water at 20 °C for 4 days. For testing of allocation to performance group D4, the specimens, after gluing, were stored under standard climatic conditions (23 °C, 50 % atmospheric humidity) for 7 days and then stored for 6 hours in boiling water, followed by 2 hours in cold water at 20 °C. Allocation to performance group D3 requires to achieve a D3-value  $\geq 2 N/mm^2$ . Allocation to performance group D4 requires to achieve a D4-value  $\geq 4 N/mm^2$  and a D3-value  $\geq 4 N/mm^2$ .

#### **Testing of cohesion at 70 °C**

As test specimens, plywood panels (made from beech wood) each 4 mm thick, 30 mm wide and 135 mm long were bonded to one another with an overlapping length of 30 mm using the adhesive dispersion tested. The glued area is 30 mm to 30 mm i.e. 900 mm<sup>2</sup>. The coating weight of adhesive applied is 100 g each side. The specimens are put together and stored for 1 minute without pressure followed by a clamping pressure of 0.2 N/mm<sup>2</sup>

applied for a time of 30 minutes. After a storage of 7 days at 23 °C/50% rel. humidity, the test specimens were stored for 4 hours at a temperature of 70 °C in an oven preheated to 70 °C. Directly following hot storage, the cohesion at 70°C was determined in a tensile shear test, in which the bonded test specimens were pulled apart using a tensile testing machine at a pulling speed of 50 mm/min and were stressed until they broke. On fracture, the maximum force  $F_{max}$  which occurred at that point was determined. The cohesion or thermal stability  $\tau$  is calculated from  $\tau = F_{max}/A$ , where A is the bonded test area. Final results are mean values from 6 single specimens and are given in N/mm<sup>2</sup>. Performance requirement is to achieve a bond strength  $\geq 4$  N/mm<sup>2</sup>.

#### Testing of cohesion at 80 °C:

As test specimens, pairs of beech wood panels each 5 mm thick, 125 mm wide and 325 mm long were bonded to one another using the respective adhesive dispersion, under a pressure distributed uniformly over the bond area. Following storage, the bonded panels were divided into test specimens each measuring 150 mm in length and 20 mm in width. After the test specimens had been prepared they were stored at a temperature of 80 °C in an oven preheated to 80 °C. Directly following hot storage, the thermal stability was determined in the tensile shear test on the lines of DIN EN 205, in which the bonded test specimens were pulled apart using a tensile testing machine at a pulling speed of 50 mm/min and were stressed until they broke. On fracture, the maximum force  $F_{max}$  which occurred at that point was determined. The cohesion or thermal stability  $\tau$  is calculated from  $\tau = F_{max}/A$ , where A is the bonded test area. Results are given in N/mm<sup>2</sup>. Performance requirement is to achieve a bond strength  $\geq 6$  N/mm<sup>2</sup>.

#### Testing the setting speed after 2.5 min setting time:

In a manner similar to the procedure for testing the bond strength, pairs of oak panels each 5 mm thick, 20 mm wide and 150 mm long were bonded using the respective adhesive dispersions, with a pressure distributed uniformly over the bond area. The bond area was 20 mm \* 20 mm. Bond strength was determined in the tensile shear test after 2.5 minutes, where after the bonded test specimens were pulled apart using a tensile testing machine at a pulling speed of 50 mm/min and were stressed until they broke. On fracture, the maximum force  $F_{max}$  which occurred at that point was determined, and was used in turn to determine the bond strength at setting time t by  $T_{\tau} = F_{max}/A$ , where A is the bonded test area.

Results are given in  $\text{N/mm}^2$ . Performance requirement is to achieve bond strength  $> 1.5 \text{ N/mm}^2$  after 2.5 min.

#### **Testing the setting speed according to the AZG-Method:**

5 During the setting of a dispersion based adhesive the strength of the bond increases. The setting can be described by measuring the change of bond strength with time. In the AZG-Method the time is determined necessary that a bonding area of  $1 \text{ cm}^2$  resists to a load of 2 N applied vertical to the bond surface. For formation of the bond  $50 \mu$  of the adhesive are applied to a standard cardboard and a  $1 \text{ cm}^2$  piece of cardboard is glued against  
10 the adhesive coating. After predetermined time the resistance of the bond against the load of 2 N is tested. As result the bond resists or it fails. The whole test is made in an automated device. The test procedure is repeated as often as necessary to find the shortest time needed to resist to the load of 2 N. This time is called AZG value. Results are given in seconds. Performance requirement is to achieve an AZG-value  $\leq 4 \text{ s}$ .

15 The following examples are given to further illustrate the present invention, but are not intended to limit the same.

#### **Examples**

20 All examples given below were executed in a 3 l glass reactor, equipped with electronic temperature measurement and control, reflux condenser, and metering pumps for at least four different feeds for parallel feeding. Mixing was achieved either by using an anchor-type stirrer at 150 rpm, constantly, or stirrer speed was increased to 180 rpm during  
25 the monomer feed period. Few experiments were carried out using a cross-beam type stirrer with inclined blades at 400 rpm.

30 The ingredients of the recipe were distributed among initial reactor charge, feed 1, feed 2, feed 3, feed 4, and feeds 5 and 6, if applied. The amount of the ingredients was chosen to give a final latex of 1800 to 2500 g. The initial reactor charge was heated and feed 1 (and 2, if used) was (were) started at approximately  $55^\circ\text{C}$  to initiate the reaction. Feeds 3 and 4 were started at  $65^\circ\text{C}$  and were metered in during 50 to 180 minutes. Reaction temperature was maintained between  $65$  and  $80^\circ\text{C}$  during the addition of feeds 3

and 4. It was up to 80 °C to 90°C for the last hour where the remaining feed 1 (and 2, if used) were added completely, after feeds 3 and 4 were finished.

The free monomer content based on latex after the start of feeds 3 and 4 was controlled by appropriate addition rates for feeds 1, 2, 3, and 4 to be between 2 to 15%. Feed 5 and 6, if applied, are added after feeds 1 and 2 have been completed. The product was cooled to ambient temperature under stirring at 100 rpm and application of a vacuum. If necessary, a small amount of defoamer was added.

### Example 1 (Comparison A)

Initial reactor charge consisted of 29 parts of a 10% PVOH solution and 12.2 parts of water. PVOH used had a weight average of molecular mass distribution of  $M_w = 103\,000$  g/Mol and a number average of  $M_n = 50\,400$  g/Mol. The average degree of hydrolysis was 89%. pH value was adjusted to 5.8 by addition of 0.02 parts of 10% NaOH. 13.1 parts of a VAC monomer were added and finally 0.08 parts of a 1% Ferro ammon sulfate solution were added just before the start of feed 1 and feed 2.

Feed 1 consisted of 2.7 parts of a 0.3% hydrogen peroxide solution and feed 2 consisted of 2.7 parts of a 1.3% SFS solution. Feed 3 consisted of 40 parts of VAC monomer. Post polymerization was done by feeds 5 and 6 consisting of 0.1 parts of a 10% tBHP and of 0.1 parts of a 10% SFS solution, respectively.

No other feeds were applied. The resulting latex (100 parts) provided a solid content of 56% for 100% monomer conversion. Reaction was executed as given above. Final latex had a Brookfield viscosity of  $Bf_{20} = 2\,600$  mPas.

### Example 2

Same as example 1, but 12.5 parts per million of 3-mercapto propionic acid (MPA) based on mass of VAC monomer was added to the initial reactor charge. The final latex had a Brookfield viscosity of  $Bf_{20} = 5\,700$  mPas. Shear thinning was improved, as indicated by the larger SF-value compared to example 1. Setting speed was improved as indicated by the drop of the AZG-value compared to example 1.

**Example 3**

Same as example 1, but 25 PPM of MPA based on mass of VAC monomer was added to the initial reactor charge. The final latex had a Brookfield viscosity of Bf20 = 6 500 mPas. Setting speed was improved as indicated by the drop of the AZG-value compared to example 1.

**Example 4 (Comparison B)**

Initial reactor charge consisted of 26 parts of a 10% PVOH solution and 16 parts of VAC monomer. PVOH used had a weight average of molecular mass distribution of  $M_w = 127\,800$  g/Mol and a number average of  $M_n = 69\,400$  g/Mol. The average degree of hydrolysis was 87%. Reaction was started at 60 °C by addition of 0.08 parts of a 20%  $H_2O_2$  solution.

Feed 1 consisted of 2.2 parts of a 0.4%  $H_2O_2$  solution. It was started 5 min after the initial  $H_2O_2$  addition together with feed 3. This feed 1 was continuously charged for 480 min. Feed 3 consisted of 46.3 parts of VAC monomer. It was fed for 360 min. Feed 4 consisted of 8.8 parts of pure water which was started 60 min after start of feed 3 and which was metered in for 240 min.

Post polymerization was done by feeds 5 and 6 consisting of 0.27 parts of a 10% tBHP and of 0.27 parts of a 10% SFS solution, respectively. Both feeds were added after feeds 1 and 2 were completed and after a 1% ferro ammon sulfate (FAS) solution of 0.07 parts was added.

No other feeds were applied. The resulting latex (100 parts) provided a solid content of 65% for 100% monomer conversion. Reaction was executed as given above. The final latex had a Brookfield viscosity of Bf20 = 33 500 mPas.

**Example 5**

Same as example 4, but 200 PPM of croton aldehyde was added to the initial reactor charge. The final latex had a Brookfield viscosity of 20 500 mPas.

**Example 6**

Same as example 4, but 400 PPM of croton aldehyde was added to the initial reactor charge. The final latex had a viscosity of  $Bf_{20} = 20\,300$  mPas.

5 **Example 7**

Same as example 4, but an effective amount of 360 PPM of propion aldehyde was added to the initial reactor charge. The final latex after dilution to 61.5% had a viscosity of 20 200 mPas.

10 **Example 8 (Comparison C)**

Initial reactor charge consisted of 37.9 parts of a 10% PVOH solution together with 6.7 parts of water. The PVOH used had a weight average of molecular mass distribution of  $M_w = 149\,200$  g/Mol and a number average of  $M_n = 94\,600$  g/Mol. The average degree of hydrolysis was 91%. pH of the aqueous solution was adjusted to 5.8 by addition of 0.05 parts of a 10% NaOH solution. Initial VAC monomer charge was 12.3 parts. Additionally 0.05 parts of a 1% FAS solution were added before starting the feeds 1 and 2.

Feed 1 consisted of 0.82 parts of a 0.25% tBHP solution, metered in for 200 min. Feed 2 consisted of 0.82 parts of a 0.38% SFS solution which was fed parallel to feed 1. Feed 3 consisted of 36.6 parts of VAC monomer which was fed in for 160 min. Feed 4 consisted of 0.3 parts of N-methylol acryl amide together with 4.3 parts of water. This was fed parallel to feed 3.

Post polymerization was done by feeds 5 and 6, consisting of 0.1 parts of a 10% tBHP solution and 0.1 parts of a 10% SFS solution, respectively. The resulting latex (100 parts) provided a solid content of 53% for 100% monomer conversion. Reaction was executed as given above. The final latex, diluted to 50% solids, had a Brookfield viscosity of  $Bf_{20} = 5\,920$  mPas.

30 **Example 9**

Same as example 8, but 25 PPM of MPA was fed within feed 4 during the reaction. The final latex, diluted to 50%, had a Brookfield viscosity  $Bf_{20} = 5\,730$  mPas.

**Example 10**

Same as example 8, but 45 PPM of MPA were fed within feed 4 during the reaction. The final latex, diluted to 50%, had a Brookfield viscosity Bf20 = 6 090 mPas.

5 **Example 11**

Same as example 8, but 90 PPM of MPA were fed within feed 4 during the reaction. The final latex, diluted to 50%, had a Brookfield viscosity Bf20 = 6 670 mPas.

**Example 12 (Comparison D)**

10 Same as example 8, but 180 PPM of MPA were fed within feed 4 during the reaction. The final latex, diluted to 50%, had a Brookfield viscosity Bf20 = 7 530 mPas.

**Example 13 (Comparison E)**

15  
20

Same as example 8, but 360 PPM of MPA were fed within feed 4 during the reaction. The final latex, diluted to 50%, had a Brookfield viscosity Bf20 = 6 870 mPas.

**Example 14 (Comparison F)**

Same as example 8, but 720 PPM of MPA were fed within feed 4 during the reaction. The final latex, diluted to 50%, had a Brookfield viscosity Bf20 = 5 400 mPas.

**Example 15 (Comparison G)**

25 Same as example 8, but instead of a anchor type stirrer a cross-beam type stirrer with inclined blades was used at 400 RPM. The final latex, diluted to 50% had a Brookfield viscosity Bf20 = 9 800 mPas. The rheological behavior clearly indicated shear thickening with a negative shear thinning factor SF.

**Example 16**

30 Same as example 15, but 25 PPM of MPA was fed within feed 4 during the reaction. The final latex, diluted to 50%, had a Brookfield viscosity Bf20 = 8 420 mPas. Shear thickening behavior of example 15 was converted to shear thinning behavior.

**Example 17 (Comparison H)**



Initial reactor charge consisted of 37.1 parts of a 10% PVOH solution together with 6.9 parts of water. The same PVOH was used as in example 16. pH of the aqueous solution was adjusted to 5.8 by addition of 0.01 parts of a 10% NaOH solution. Initial VAC monomer charge was 12 parts. Additionally 0.05 parts of a 1% FAS solution were added just before start of feeds 1 and 2.

Feed 1 consisted of 2 parts of a 0.25% tBHP solution, metered in for 200 min. Feed 2 consisted of 2 parts of a 0.38% SFS solution which was fed parallel to feed 1. Feed 3 consisted of 35.83 parts of VAC monomer and was metered in for 160 min. Feed 4 consisted of 0.9 parts of N-methylol acryl amide together with 3 parts of water. This was fed parallel to feed 3.

Post polymerization was done by feeds 5 and 6, consisting of 0.1 parts of a 10% tBHP solution and 0.1 parts of a 10% SFS solution, respectively. The resulting latex (100 parts) provided a solid content of 52.5% for 100% monomer conversion. Reaction was executed as given above. The final latex, diluted to 50% solids, had a Brookfield viscosity of  $Bf_{20} = 16\,730$  mPas. Rheological behavior indicated strong shear thickening with a negative shear thinning factor SF.

### Example 18

Same as example 17, but 25 PPM of MPA was fed within feed 4 during the reaction. Final latex, diluted to 50%, had a Brookfield viscosity  $Bf_{20} = 10\,060$  mPas. The shear thickening behavior of example 17 was converted to shear thinning behavior.

**Example 19**

Same as example 18, but monomer feed 3 comprised by 95% of VAC and 5% of VeoVa9 monomer (last supplied by Shell). The final latex, diluted to 50% solids, had a Brookfield viscosity of Bf20 = 9 050 mPas.

5

**Example 20 (Comparison I)**

Same as example 17, but monomer feed 3 comprised by 85% of VAC and 15% of VeoVa9 monomer. The final latex, diluted to 50% solids, had a Brookfield viscosity of Bf20 = 10 800 mPas.

10

**Example 21**

Same as example 20, but 25 PPM of MPA was fed within feed 4 during the reaction. The final latex, diluted to 50% solids, had a Brookfield viscosity of Bf20 = 8 660 mPas.

15

**Example 22**

Same as example 21, but NMA content in feed 3 was raised from 0.9 parts to 1.05 parts. The final latex, diluted to 50% solids, had a Brookfield viscosity of Bf20 = 8 000 mPas.

20

P  
O  
L  
Y  
M  
E  
R  
S  
I  
N  
T  
H  
E  
F  
I  
E  
L  
D

**Table 1: Latex and Adhesive Performance**

| Example | CTA<br>PPM         | final<br>particle<br>size<br>nm | K<br>Value | s.c.<br>% | Bf20<br>mPas | SF     | setting speed     |                                      | cohesion                           |                                    |
|---------|--------------------|---------------------------------|------------|-----------|--------------|--------|-------------------|--------------------------------------|------------------------------------|------------------------------------|
|         |                    |                                 |            |           |              |        | paper<br>AZG<br>s | wood<br>2.5 min<br>N/mm <sup>2</sup> | wood<br>70 °C<br>N/mm <sup>2</sup> | wood<br>80 °C<br>N/mm <sup>2</sup> |
| 1 A     | 0                  | 1 187 <sup>1)</sup>             | 115        | 56        | 2 600        | 0.65   | 6.0               | --                                   | 4.6                                | --                                 |
| 2       | 12.5 <sup>A)</sup> | 932 <sup>1)</sup>               | 134        | 56        | 5 700        | 1.13   | 3.8               | --                                   | 4.4                                | --                                 |
| 3       | 25.0 <sup>A)</sup> | 907 <sup>1)</sup>               | 132        | 56        | 6 500        | 1.19   | 3.0               | --                                   | 4.3                                | --                                 |
| 4 B     | 0                  | 1 551 <sup>2)</sup>             | 112        | 65        | 33 500       | 0.80   | 5.7               | --                                   | 4.5                                | --                                 |
| 5       | 200 <sup>B)</sup>  | 1 357 <sup>2)</sup>             | 113        | 65        | 20 500       | 0.92   | 2.7               | --                                   | 4.5                                | --                                 |
| 6       | 400 <sup>B)</sup>  | 1 112 <sup>2)</sup>             | 107        | 65        | 20 300       | 1.02   | 3.7               | --                                   | 4.2                                | --                                 |
| 7       | 360 <sup>C)</sup>  | 1 283 <sup>2)</sup>             | 96         | 61.5      | 20 200       | 1.45   | 3.5               |                                      | 4.0                                |                                    |
| 8 C     | 0                  | 935 <sup>1)</sup>               | 136        | 50        | 5 920        | 0.25   | --                | 1.5                                  | --                                 | 7.2                                |
| 9       | 25 <sup>A)</sup>   | 822 <sup>1)</sup>               | 142        | 50        | 5 730        | 0.30   | --                | 1.9                                  | --                                 | 7.0                                |
| 10      | 45 <sup>A)</sup>   | 777 <sup>1)</sup>               | 135        | 50        | 6 090        | 0.45   | --                | 2.0                                  | --                                 | 7.2                                |
| 11      | 90 <sup>A)</sup>   | 760 <sup>1)</sup>               | 117        | 50        | 6 670        | 0.54   | --                | 2.0                                  | --                                 | 6.5                                |
| 12 D    | 180 <sup>A)</sup>  | 743 <sup>1)</sup>               | 102        | 50        | 7 530        | 0.64   | --                | 2.1                                  | --                                 | 5.5                                |
| 13 E    | 360 <sup>A)</sup>  | 1 050 <sup>1)</sup>             | 91         | 50        | 6 870        | 0.39   | --                | 2.3                                  | --                                 | 5.1                                |
| 14 F    | 720 <sup>A)</sup>  | 1 045 <sup>1)</sup>             | 76         | 50        | 5 400        | 0.40   | --                | 2.0                                  | --                                 | 5.2                                |
| 15 G    | 0                  | 1 440 <sup>1)</sup>             | 134        | 50        | 9 800        | - 0.16 | --                | 1.5                                  | --                                 | 7.2                                |
| 16      | 25 <sup>D)</sup>   | 1 020 <sup>1)</sup>             | 145        | 50        | 8 420        | 0.15   | --                | 1.8                                  | --                                 | 7.3                                |
| 17 H    | 0                  | 1 950 <sup>2)</sup>             | 136        | 50        | 16 730       | - 0.24 | --                | 1.1                                  | --                                 | 7.4                                |
| 18      | 25 <sup>A)</sup>   | 1 050 <sup>2)</sup>             | 131        | 50        | 10 060       | 0.21   |                   | 2.0                                  |                                    | 7.5                                |
| 19      | 25 <sup>A)</sup>   | 1 236 <sup>2)</sup>             | 123        | 50        | 9 050        | 0.15   | --                | 2.4                                  | --                                 | 7.2                                |
| 20 I    | 0                  | 1 176 <sup>2)</sup>             | 119        | 50        | 10 800       | 0.08   | --                | 1.7                                  | --                                 | 6.8                                |
| 21      | 25 <sup>A)</sup>   | 1 226 <sup>2)</sup>             | 124        | 50        | 8 660        | 0.21   | --                | 2.8                                  | --                                 | 7.1                                |
| 22      | 25 <sup>A)</sup>   | 1 170 <sup>2)</sup>             | 126        | 50        | 8 000        | 0.31   | --                | 2.2                                  | --                                 | 7.1                                |

A) CTA: 3-mercato propionic acid

B) CTA: croton aldehyde

C) CTA: propion aldehyde

D) CTA: 2-mercapto propionic acid

<sup>1)</sup> particle size median x<sub>3,50</sub> from COULTER LS 230 analysis<sup>2)</sup> particle size weight average from COULTER N4 analysis

**Table 2: Wood Glue Performance**

| Example | D3-value<br>N / mm <sup>2</sup> | D4-value<br>N / mm <sup>2</sup> |
|---------|---------------------------------|---------------------------------|
| 9       | 2.8                             | --                              |
| 10      | 3.0                             | --                              |
| 11      | 2.9                             | --                              |
| 16      | 2.3                             | 1.8                             |
| 18      | 3.4                             | 3.1                             |
| 19      | 3.9                             | 3.0                             |
| 21      | 5.3                             | 4.1                             |
| 22      | 5.5                             | 4.0                             |

In Table 1 the results of the 13 examples, and 9 comparative examples are summarized. Table 2 summarizes results obtained for the water resistance of the bond when base emulsions obtained in the framework of this invention were formulated as wood glues.

Examples 2, 3, 5, 6, and 7 represent VAC homopolymer latices of this invention prepared in the presence of PVOH. The comparison with Example 1 reveals that the use of trace amounts of CTA results in the following: the setting speed measured as AZG is considerably increased, the shear thinning may be adjusted within the required range, cohesion stays within its desired range and K-value is slightly increased or remains about unchanged.

Examples 9, 10, 11, 16, 18, 19, 21, and 22 represent VAC co-polymers suitable as base of high performance water resistant D3 wood glues. Comparing Example 16 with 15G, and 18 with 17H it is obvious that the use of trace amounts of a CTA may even convert a shear thickening behavior ( $SF < 0$ ) to a shear thinning one ( $SF > 0$ ) within the desired range of SF. At the same time the setting speed is improved without impairing cohesion.

Additionally, the results of the comparative Examples 12D, 13E, 14F demonstrate, that use of a CTA above the limits of this invention in accordance with the prior art will result in a much higher decrease of the average molecular weight, expressed as the K-value, and will thereby contribute to an unacceptable loss or reduction of cohesion.

5

Examples 21 and 22 represent VAC co-polymers suitable as a base of high performance boiling water resistant D4 wood glues. Comparing Examples 21 and 22 with 20I, both the setting speed and the shear thinning are improved by use trace amounts of a CTA.

10

11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68  
69  
70  
71  
72  
73  
74  
75  
76  
77  
78  
79  
80  
81  
82  
83  
84  
85  
86  
87  
88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100  
101  
102  
103  
104  
105  
106  
107  
108  
109  
110  
111  
112  
113  
114  
115  
116  
117  
118  
119  
120  
121  
122  
123  
124  
125  
126  
127  
128  
129  
130  
131  
132  
133  
134  
135  
136  
137  
138  
139  
140  
141  
142  
143  
144  
145  
146  
147  
148  
149  
150  
151  
152  
153  
154  
155  
156  
157  
158  
159  
160  
161  
162  
163  
164  
165  
166  
167  
168  
169  
170  
171  
172  
173  
174  
175  
176  
177  
178  
179  
180  
181  
182  
183  
184  
185  
186  
187  
188  
189  
190  
191  
192  
193  
194  
195  
196  
197  
198  
199  
200  
201  
202  
203  
204  
205  
206  
207  
208  
209  
210  
211  
212  
213  
214  
215  
216  
217  
218  
219  
220  
221  
222  
223  
224  
225  
226  
227  
228  
229  
230  
231  
232  
233  
234  
235  
236  
237  
238  
239  
240  
241  
242  
243  
244  
245  
246  
247  
248  
249  
250  
251  
252  
253  
254  
255  
256  
257  
258  
259  
260  
261  
262  
263  
264  
265  
266  
267  
268  
269  
270  
271  
272  
273  
274  
275  
276  
277  
278  
279  
280  
281  
282  
283  
284  
285  
286  
287  
288  
289  
290  
291  
292  
293  
294  
295  
296  
297  
298  
299  
300  
301  
302  
303  
304  
305  
306  
307  
308  
309  
310  
311  
312  
313  
314  
315  
316  
317  
318  
319  
320  
321  
322  
323  
324  
325  
326  
327  
328  
329  
330  
331  
332  
333  
334  
335  
336  
337  
338  
339  
340  
341  
342  
343  
344  
345  
346  
347  
348  
349  
350  
351  
352  
353  
354  
355  
356  
357  
358  
359  
360  
361  
362  
363  
364  
365  
366  
367  
368  
369  
370  
371  
372  
373  
374  
375  
376  
377  
378  
379  
380  
381  
382  
383  
384  
385  
386  
387  
388  
389  
390  
391  
392  
393  
394  
395  
396  
397  
398  
399  
400  
401  
402  
403  
404  
405  
406  
407  
408  
409  
410  
411  
412  
413  
414  
415  
416  
417  
418  
419  
420  
421  
422  
423  
424  
425  
426  
427  
428  
429  
430  
431  
432  
433  
434  
435  
436  
437  
438  
439  
440  
441  
442  
443  
444  
445  
446  
447  
448  
449  
450  
451  
452  
453  
454  
455  
456  
457  
458  
459  
460  
461  
462  
463  
464  
465  
466  
467  
468  
469  
470  
471  
472  
473  
474  
475  
476  
477  
478  
479  
480  
481  
482  
483  
484  
485  
486  
487  
488  
489  
490  
491  
492  
493  
494  
495  
496  
497  
498  
499  
500  
501  
502  
503  
504  
505  
506  
507  
508  
509  
510  
511  
512  
513  
514  
515  
516  
517  
518  
519  
520  
521  
522  
523  
524  
525  
526  
527  
528  
529  
530  
531  
532  
533  
534  
535  
536  
537  
538  
539  
540  
541  
542  
543  
544  
545  
546  
547  
548  
549  
550  
551  
552  
553  
554  
555  
556  
557  
558  
559  
560  
561  
562  
563  
564  
565  
566  
567  
568  
569  
570  
571  
572  
573  
574  
575  
576  
577  
578  
579  
580  
581  
582  
583  
584  
585  
586  
587  
588  
589  
590  
591  
592  
593  
594  
595  
596  
597  
598  
599  
600  
601  
602  
603  
604  
605  
606  
607  
608  
609  
610  
611  
612  
613  
614  
615  
616  
617  
618  
619  
620  
621  
622  
623  
624  
625  
626  
627  
628  
629  
630  
631  
632  
633  
634  
635  
636  
637  
638  
639  
640  
641  
642  
643  
644  
645  
646  
647  
648  
649  
650  
651  
652  
653  
654  
655  
656  
657  
658  
659  
660  
661  
662  
663  
664  
665  
666  
667  
668  
669  
670  
671  
672  
673  
674  
675  
676  
677  
678  
679  
680  
681  
682  
683  
684  
685  
686  
687  
688  
689  
690  
691  
692  
693  
694  
695  
696  
697  
698  
699  
700  
701  
702  
703  
704  
705  
706  
707  
708  
709  
710  
711  
712  
713  
714  
715  
716  
717  
718  
719  
720  
721  
722  
723  
724  
725  
726  
727  
728  
729  
730  
731  
732  
733  
734  
735  
736  
737  
738  
739  
740  
741  
742  
743  
744  
745  
746  
747  
748  
749  
750  
751  
752  
753  
754  
755  
756  
757  
758  
759  
760  
761  
762  
763  
764  
765  
766  
767  
768  
769  
770  
771  
772  
773  
774  
775  
776  
777  
778  
779  
780  
781  
782  
783  
784  
785  
786  
787  
788  
789  
790  
791  
792  
793  
794  
795  
796  
797  
798  
799  
800  
801  
802  
803  
804  
805  
806  
807  
808  
809  
810  
811  
812  
813  
814  
815  
816  
817  
818  
819  
820  
821  
822  
823  
824  
825  
826  
827  
828  
829  
830  
831  
832  
833  
834  
835  
836  
837  
838  
839  
840  
841  
842  
843  
844  
845  
846  
847  
848  
849  
850  
851  
852  
853  
854  
855  
856  
857  
858  
859  
860  
861  
862  
863  
864  
865  
866  
867  
868  
869  
870  
871  
872  
873  
874  
875  
876  
877  
878  
879  
880  
881  
882  
883  
884  
885  
886  
887  
888  
889  
890  
891  
892  
893  
894  
895  
896  
897  
898  
899  
900  
901  
902  
903  
904  
905  
906  
907  
908  
909  
910  
911  
912  
913  
914  
915  
916  
917  
918  
919  
920  
921  
922  
923  
924  
925  
926  
927  
928  
929  
930  
931  
932  
933  
934  
935  
936  
937  
938  
939  
940  
941  
942  
943  
944  
945  
946  
947  
948  
949  
950  
951  
952  
953  
954  
955  
956  
957  
958  
959  
960  
961  
962  
963  
964  
965  
966  
967  
968  
969  
970  
971  
972  
973  
974  
975  
976  
977  
978  
979  
980  
981  
982  
983  
984  
985  
986  
987  
988  
989  
990  
991  
992  
993  
994  
995  
996  
997  
998  
999  
1000  
1001  
1002  
1003  
1004  
1005  
1006  
1007  
1008  
1009  
1010  
1011  
1012  
1013  
1014  
1015  
1016  
1017  
1018  
1019  
1020  
1021  
1022  
1023  
1024  
1025  
1026  
1027  
1028  
1029  
1030  
1031  
1032  
1033  
1034  
1035  
1036  
1037  
1038  
1039  
1040  
1041  
1042  
1043  
1044  
1045  
1046  
1047  
1048  
1049  
1050  
1051  
1052  
1053  
1054  
1055  
1056  
1057  
1058  
1059  
1060  
1061  
1062  
1063  
1064  
1065  
1066  
1067  
1068  
1069  
1070  
1071  
1072  
1073  
1074  
1075  
1076  
1077  
1078  
1079  
1080  
1081  
1082  
1083  
1084  
1085  
1086  
1087  
1088  
1089  
1090  
1091  
1092  
1093  
1094  
1095  
1096  
1097  
1098  
1099  
1100  
1101  
1102  
1103  
1104  
1105  
1106  
1107  
1108  
1109  
1110  
1111  
1112  
1113  
1114  
1115  
1116  
1117  
1118  
1119  
1120  
1121  
1122  
1123  
1124  
1125  
1126  
1127  
1128  
1129  
1130  
1131  
1132  
1133  
1134  
1135  
1136  
1137  
1138  
1139  
1140  
1141  
1142  
1143  
1144  
1145  
1146  
1147  
1148  
1149  
1150  
1151  
1152  
1153  
1154  
1155  
1156  
1157  
1158  
1159  
1160  
1161  
1162  
1163  
1164  
1165  
1166  
1167  
1168  
1169  
1170  
1171  
1172  
1173  
1174  
1175  
1176  
1177  
1178  
1179  
1180  
1181  
1182  
1183  
1184  
1185  
1186  
1187  
1188  
1189  
1190  
1191  
1192  
1193  
1194  
1195  
1196  
1197  
1198  
1199  
1200  
1201  
1202  
1203  
1204  
1205  
1206  
1207  
1208  
1209  
1210  
1211  
1212  
1213  
1214  
1215  
1216  
1217  
1218  
1219  
1220  
1221  
1222  
1223  
1224  
1225  
1226  
1227  
1228  
1229  
1230  
1231  
1232  
1233  
1234  
1235  
1236  
1237  
1238  
1239  
1240  
1241  
1242  
1243  
1244  
1245  
1246  
1247  
1248  
1249  
1250  
1251  
1252  
1253  
1254  
1255  
1256  
1257  
1258  
1259  
1260  
1261  
1262  
1263  
1264  
1265  
1266  
1267  
1268  
1269  
1270  
1271  
1272  
1273  
1274  
1275  
1276  
1277  
1278  
1279  
1280  
1281  
1282  
1283  
1284  
1285  
1286  
1287  
1288  
1289  
1290  
1291  
1292  
1293  
1294  
1295  
1296  
1297  
1298  
1299  
1300  
1301  
1302  
1303  
1304  
1305  
1306  
1307  
1308  
1309  
1310  
1311  
1312  
1313  
1314  
1315  
1316  
1317  
1318  
1319  
1320  
1321  
1322  
1323  
1324  
1325  
1326  
1327  
1328  
1329  
1330  
1331  
1332  
1333  
1334  
1335  
1336  
1337  
1338  
1339  
1340  
1341  
1342  
1343  
1344  
1345  
1346  
1347  
1348  
1349  
1350  
1351  
1352  
1353  
1354  
1355  
1356  
1357  
1358  
1359  
1360  
1361  
1362  
1363  
1364  
1365  
1366  
1367  
1368  
1369  
1370  
1371  
1372  
1373  
1374  
1375  
1376  
1377  
1378  
1379  
1380  
1381  
1382  
1383  
1384  
1385  
1386  
1387  
1388  
1389  
1390  
1391  
1392  
1393  
1394  
1395  
1396  
1397  
1398  
1399  
1400  
1401  
1402  
1403  
1404  
1405  
1406  
1407  
1408  
1409  
1410  
1411  
1412  
1413  
1414  
1415  
1416  
1417  
1418  
1419  
1420  
1421  
1422  
1423  
1424  
1425  
1426  
1427  
1428  
1429  
1430  
1431  
1432  
1433  
1434  
1435  
1436  
1437  
1438  
1439  
1440  
1441  
1442  
1443  
1444  
1445  
1446  
1447  
1448  
1449  
1450  
1451  
1452  
1453  
1454  
1455  
1456  
1457  
1458  
1459  
1460  
1461  
1462  
1463  
1464  
1465  
1466  
1467  
1468  
1469  
1470  
1471  
1472  
1473  
1474  
1475  
1476  
1477  
1478  
1479  
1480  
1481  
1482  
1483  
1484  
1485  
1486  
1487  
1488  
1489  
1490  
1491  
1492  
1493  
1494  
1495  
1496  
1497  
1498  
1499  
1500  
1501  
1502  
1503  
1504  
1505  
1506  
1507  
1508  
1509  
1510  
1511  
1512  
1513  
1514  
1515  
1516  
1517  
1518  
1519  
1520  
1521  
1522  
1523  
1524  
1525  
1526  
1527  
1528  
1529  
1530  
1531  
1532  
1533  
1534  
1535  
1536  
1537  
1538  
1539  
1540  
1541  
1542  
1543  
1544  
1545  
1546  
1547  
1548  
1549  
1550  
1551  
1552  
1553  
1554  
1555  
1556  
1557  
1558  
1559  
1560  
1561  
1562  
1563  
1564  
1565  
1566  
1567  
1568  
1569  
1570  
1571  
1572  
1573  
1574  
1575  
1576  
1577  
1578  
1579  
1580  
1581  
1582  
1583  
1584  
1585  
1586  
1587  
1588  
1589  
1590  
1591  
1592  
1593  
1594  
1595  
1596  
1597  
1598  
1599  
1600  
1601  
1602  
1603  
1604  
1605  
1606  
1607  
1608  
1609  
1610  
1611  
1612  
1613  
1614  
1615  
1616  
1617  
1618  
1619  
1620  
1621  
1622  
1623  
1624  
1625  
1626  
1627  
1628  
1629  
1630  
1631  
1632  
1633  
1634  
1635  
1636  
1637  
1638  
1639  
1640  
1641  
1642  
1643  
1644  
1645  
1646  
1647  
1648  
1649  
1650  
1651  
1652  
1653  
1654  
1655  
1656  
1657  
1658  
1659  
1660  
1661  
1662  
1663  
1664  
1665  
1666  
1667  
1668  
1669  
1670  
1671  
1672  
1673  
1674  
1675  
1676  
1677  
1678  
1679  
1680  
1681  
1682  
1683  
1684  
1685  
1686  
1687  
1688  
1689  
1690  
1691  
1692  
1693  
1694  
1695  
1696  
1697  
1698  
1699  
1700  
1701  
1702  
1703  
1704  
1705  
1706  
1707  
1708  
1709  
1710  
1711  
1712  
1713  
1714  
1715  
1716  
1717  
1718  
1719  
1720  
1721  
1722  
1723  
1724  
1725  
1726  
1727  
1728  
1729  
1730  
1731  
1732  
1733  
1734  
1735  
1736  
1737  
1738  
1739  
1740  
1741  
1742  
1743  
1744  
1745  
1746  
1747  
1748  
1749  
1750  
1751  
1752  
1753  
1754  
1755  
1756  
1757  
1758  
1759  
1760  
1761  
1762  
1763  
1764  
1765  
1766  
1767  
1768  
1769  
1770  
1771  
1772  
1773  
1774  
1775  
1776  
1777  
1778  
1779  
1780  
1781  
1782  
1783  
1784  
1785  
1786  
1787  
1788  
1789  
1790  
1791  
1792  
1793  
1794  
1795  
1796  
1797  
1798  
1799  
1800  
1801  
1802  
1803  
1804  
1805  
1806  
1807  
1808  
1809  
1810  
1811  
1812  
1813  
1814  
1815  
1816  
1817  
1818  
1819  
1820  
1821  
1822  
1823  
1824  
1825  
1826  
1827  
1828  
1829  
1830  
1831  
1832  
1833  
1834  
1835  
1836  
1837  
1838  
1839  
1840  
1841  
1842  
1843  
1844  
1845  
1846  
1847  
1848  
1849  
1850  
1851  
1852  
1853  
1854  
1855  
1856  
1857  
1858  
1859  
1860  
1861  
1862  
1863  
1864  
1865  
1866  
1867  
1868  
1869  
1870  
1871  
1872  
1873  
1874  
1875  
1876  
1877  
1878  
1879  
1880  
1881  
1882  
1883  
1884  
1885  
1886  
1887  
1888  
1889  
1890  
1891  
1892  
1893  
1894  
1895  
1896  
1897  
1898  
1899  
1900  
1901  
1902  
1903  
1904  
1905  
1906  
1907  
1908  
1909  
1910  
1911  
1912  
1913  
1914  
1915  
1916  
1917  
1918  
1919  
1920  
1921  
1922  
1923  
1924  
1925  
1926  
1927  
1928  
1929  
1930  
1931  
1932  
1933  
1934  
1935  
1936  
1937  
1938  
1939  
1940  
1941  
1942  
1943  
1944  
1945  
1946  
1947  
1948  
1949  
1950  
1951  
1952  
1953  
1954  
1955  
1956  
1957  
1958  
1959  
1960  
1961  
1962  
1963  
1964  
1965  
1966  
1967  
1968  
1969  
1970  
1971  
1972  
1973  
1974  
1975  
1976  
1977  
1978  
1979  
1980  
1981  
1982  
1983  
1984  
1985  
1986  
1987  
1988  
1989  
1990  
1991  
1992  
1993  
1994  
1995  
1996  
1997  
1998  
1999  
2000  
2001  
2002  
2003  
2004  
2005  
2006  
2007  
2008  
2009  
2010  
2011  
2012  
2013  
2014  
2015  
2016  
2017  
2018  
2019  
2020  
2021  
2022  
2023  
2024  
2025  
2026  
2027  
2028  
2029  
2030  
2031  
2032  
2033  
2034  
2035  
2036  
2037  
2038  
2039  
2040  
2041  
2042  
2043  
2044  
2045  
2046  
2047  
2048  
2049  
2050  
2051  
2052  
2053  
2054  
2055  
2056  
2057  
2058  
2059  
2060  
2061  
2062  
2063  
2064  
2065  
2066  
2067  
2068  
2069  
2070  
2071  
2072  
2073  
2074  
2075  
2076  
2077  
2078  
2079  
2080  
2081  
2082  
2083  
2084  
2085  
2086  
2087  
2088  
2089  
2090  
2091  
2092  
2093  
2094  
2095  
2096  
2097  
2098  
2099  
2100  
2101  
2102  
2103  
2104  
2105  
2106  
2107  
2108  
2109  
2110  
2111  
2112  
2113  
2114  
2115  
2116  
2117  
2118  
2119  
2120  
2121  
2122  
2123  
2124  
2125  
2126  
2127  
2128  
2129  
2130  
2131  
2132  
2133  
2134  
2135  
2136  
2137  
2138  
2139  
2140  
2141  
2142  
2143  
2144  
2145  
2146  
2147  
2148  
2149  
2150  
2151  
2152  
2153  
2154  
2155  
2156  
2157  
2158  
2159  
2160  
2161  
2162  
2163  
2164  
2165  
2166  
2167  
2168  
2169  
2170  
2171  
2172  
2173  
2174  
2175  
2176  
2177  
2178  
2179  
2180  
2181  
2182  
2183  
2184  
2185  
2186  
2187  
2188  
2189  
2190  
2191  
2192  
2193  
2194  
2195  
2196  
2197  
2198  
2199  
2200